With compliments of
Chas. H. Herty.

THE DOUBLE HALIDES

OF

LEAD AND THE ALKALI METALS.

LC

A DISSERTATION

PRESENTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

CHARLES H. HERTY.

1890.

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ON THE DOUBLE HALIDES OF LEAD.[1]

INTRODUCTION.

At one time a sharp distinction was drawn between the oxygen acids and bases. But now this sharp distinction no longer holds good, for many substances act either as acid or base according to the nature of the substance with which it combines: thus aluminium hydroxide when treated with strong acids acts as a base, giving rise to aluminium salts of the acids, but when treated with strong bases it acts as an acid, giving rise to a class of compounds called aluminates. In fact, the oxygen compounds form a continuous series, in which, beginning with the strongest bases, the basic properties gradually diminish while the acid properties increase.

Just as the acidic oxides combine with the basic oxides to form salts, so, according to Von Bonsdorff,[2] should acidic halides combine with basic halides to form compounds analogous to the oxygen salts. In the same year, 1826, Boullay[3] called attention to the similarity between the oxides, halides and sulphides, and put forward the view that just as oxygen acids and bases combine to form oxygen salts, so halides combine with each other to form true salts, and similarly sulphides combine with each other to form sulpho salts. In 1840, Dr. Hare, of Philadelphia, in his Compendium, recognised the close analogy between the oxy, sulpho, chloro, bromo, and iodo salts.

But these views of Von Bonsdorff, Boullay and Hare were not generally accepted. The majority of chemists rested satisfied with considering these bodies molecular compounds and not true

[1] ACKNOWLEDGMENT.—The author of this dissertation desires to express his most sincere thanks to Professor Remsen, at whose suggestion the work was undertaken, and with whose constant advice it has been conducted.

The author desires to express his thanks also to Doctors Morse and Renouf for valuable instruction, and finally to Doctors Williams and Clark, under whom the course in mineralogy and geology was pursued.

[2] Ann. chim. phys. [2], **34**, 142.

[3] Ibid. [2], **34**, 337.

chemical compounds. In accordance with this idea they expressed the composition of these bodies in the following manner:

$$PbI_2.KI$$
$$MgCl_2.KCl$$
$$AlF_3.3NaF,$$

Professor Remsen,[1] of the Johns Hopkins University, in an extended article on the "Nature and Structure of the Double Halides," has shown that from an examination of the composition of this large class of compounds the following law may be deduced: "When a halide of any element combines with a halide of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater, and is generally less, than the number of halogen atoms contained in the latter." In view of the facts embraced under this law, and the close analogy between the act involved in the formation of the double halides and that of the oxygen salts, and further, the similarity between the products so formed, he offers the following explanation for these compounds: "Two halogen atoms can play the same part that the so-called linking oxygen atom plays in oxygen salts."

This view has been held by chemists in more or less modified form for some time. Naquet[2] in 1867 was the first to offer this explanation. He explained the compound of silver chloride and potassium chloride by the formula

$$\begin{matrix} Ag \\ K \end{matrix} > \overset{II}{Cl_2},$$

according to which the chlorine acts as a bivalent element. Blomstrand[3] in 1869 offered a somewhat similar formula for the double chloride of magnesium and potassium, thus,

$$Mg < \begin{matrix} Cl = \overset{III}{Cl}K, \\ Cl \end{matrix}$$

the chlorine here acting as a trivalent element.

If the view be accepted that the halogen atoms can play the same part as the linking oxygen atom, then a remarkably close

[1] Am. Chem. J. **11**, 291.

[2] Principes de Chimie fondée sur les Theories Modernes.

[3] Die Chemie der Jetztzeit vom Standpunkte der electro-chemischen Auffassung aus Berzelius Lehre entwickelt.

analogy is seen to exist between the oxgen salts and the double halides, thus,

$$Al\begin{cases}(Cl_2)Na\\(Cl_2)Na\\(Cl_2)Na\end{cases} \qquad Al\begin{cases}ONa\\ONa\\ONa\end{cases}$$

$$Si\begin{cases}F\\F\\(F_2)K\\(F_2)K\end{cases} \qquad Si\begin{cases}O\\OK\\OK\end{cases}$$

The principal objection urged against this view is that emphasised by Professor Horstmann,[1] namely, that the halogen atoms must be considered to act as bivalent elements. But this cannot long stand in view of the existence of such compounds as ICl_3, IF_5, etc. Furthermore, the halogens have been shown to be polyvalent toward oxygen. Therefore it is difficult to see why this objection should be urged any longer.

On reading the article in Graham-Otto's "Lehrbuch der anorganischen Chemie," on the combinations of lead iodide with potassium iodide, one cannot fail to be impressed with the fact that the different combinations of these bodies form a marked exception to the above mentioned law. In addition to the salts $KPbI_3$ ($PbI_2.KI$) and K_2PbI_4 ($PbI_2.2KI$) there are mentioned also the salts $K_4Pb_3I_{10}$ ($3PbI_2.4KI$), K_4PbI_6 ($PbI_2.4KI$), and K_5PbI_7 ($PbI_2.5KI$).

In view of these facts this investigation was undertaken to determine whether the combinations of lead iodide with potassium iodide really form an exception to the above law. In order to do this all the previous work on this subject was carefully repeated, and the conditions of the several experiments varied in every way possible. The investigation was then extended to the corresponding chlorine and bromine compounds, in regard to which little was known. It was hoped that the work could be extended to the fluorine compounds and to mixed compounds containing more than one halogen, but this could not be accomplished on account of lack of time. It is hoped that in the future this portion of the investigation can be completed.

Method of Analysis.

It is peculiar that in giving the results of their work on the double iodides of lead and potassium neither Berthelot nor

[1] Lehrbuch der physikalischen und theoretischen Chemie.

Ditte give the methods used by them for the analysis of the salts, although results are given by each for complete analyses. It is difficult to decide just what conclusion to draw from this fact. To say the least of it, and to look at it in the most charitable light, one would be led to suppose that the analyses of the salts must be such a simple matter that it does not deserve to be mentioned. However, this is far from being the case, as after working on the subject for two years it must be confessed that as yet no absolutely trustworthy method for complete analysis has been found. The composition of most of the salts prepared in this investigation was deduced from the determinations of water of crystallisation and lead. The water was determined by heating to 110° for three hours a portion of the salt thoroughly dried by pressing between drying paper. In another portion the lead was determined thus: A weighed portion of the salt (about 1 gram) was introduced into an Erlenmeyer flask of 125 cc. capacity. Sulphuric acid sufficient to decompose the salt was then introduced into the flask, which was then inclined in order to prevent loss by sputtering, and a gentle heat applied until all the iodine was driven off. The lead and potassium are now in the form of sulphates. A close examination of the flask now shows that small yellow particles of lead iodide remain undecomposed on the sides of the flask. These were then washed down with concentrated sulphuric acid, and the mass thoroughly boiled for about an hour longer in order to insure the conversion of all the lead into sulphate. After cooling, the mass was diluted with water to about 100 cc. and a small quantity of alcohol to prevent any lead sulphate being dissolved. The whole was then allowed to stand until the supernatant liquid became perfectly clear, when it was filtered through a Gooch crucible. The lead sulphate was then washed thoroughly first with water to which a little sulphuric acid and alcohol had been added, in order to remove all traces of potassium sulphate, then washed with water containing a little alcohol in order to remove all sulphuric acid. The crucible was then dried thoroughly at 110° and finally heated to a low red heat, allowed to cool in a desiccator for twenty minutes and weighed. To determine the potassium by simple evaporation of the filtrate containing potassium sulphate and sulphuric acid is not practicable on account of the large excess of sulphuric acid necessarily present. Experiments were made on the separation of lead as sulphide by hydrogen sulphide,

but it was found that in every case some of the lead sulphide remained in solution, in consequence most probably of the presence of the alkali halide. Various other methods were tried, all of which proved of no value.

The method finally adopted for complete analysis is as follows:

1. In one portion of the salt, water of crystallisation was determined by heating in an air-bath for three hours at 110°.

2. In a second portion, lead was determined by conversion into the sulphate, as described above.

3. In a third portion, iodine and potassium were determined thus: about 1 gram of the salt was treated with 100 cc. water in a small beaker. This was stirred thoroughly in order to insure complete decomposition of the salt, and filtered through a Gooch crucible *without washing*, for if water be added to the filtrate lead iodide separates. The iodine in the filtrate was then precipitated as silver iodide. The residue on the Gooch crucible was then washed with cold water, and the washings again passed through the crucible in order to retain any lead iodide which may have separated, and to insure all potassium iodide being removed from the crucible. This second filtrate was then added to the first, in which silver nitrate was present in excess. The silver iodide was then washed, dried and weighed. The lead iodide on the crucible was then dried and weighed. From the combined results of lead iodide and silver iodide the total amount of iodine was calculated.

4. The filtrate from the silver iodide was then treated with hydrogen sulphide in order to remove all lead and silver, filtered and evaporated to dryness with a little sulphuric acid. The residue of potassium sulphate was then heated to redness, allowed to cool, and weighed. From this the weight of potassium was calculated.

Analysed according to the above described method, the crystalline salt, obtained by dissolving lead iodide in a hot solution of potassium iodide (saturated at 22°) and allowing to cool, gave the following results:

I. 1.2486 gram salt lost 0.0683 gram H_2O.

II. 0.8166 gram salt gave 0.3687 gram $PbSO_4$ = 0.2518 gram Pb.

III. 1.4549 gram salt gave 0.9057 gram PbI_2 = 0.4989 gram I, and 0.622 gram AgI = 0.3361 gram I. (Total I = 0.8350 gram.)

IV. 1.4549 gram salt gave 0.2018 gram K_2SO_4 = 0.0906 gram K.

	Calculated for $KPbI_3.2H_2O$.	Found.
Pb	31.23	30.84
I	57.43	57.39
K	5.91	6.23
H_2O	5.43	5.47

This salt was evidently the salt $KPbI_3.2H_2O$. As this analysis proved that the methods for determining water of crystallisation and lead were reliable, therefore all the salts were identified by the determinations of water and lead. In all the calculations the atomic weights given by Meyer and Seubert were used.

Potassium Iodoplumbite.

I. *Salt of the composition* $KPbI_3.2H_2O$ ($PbI_2.KI.2H_2O$). The first work on the subject of the combinations of lead iodide with potassium iodide was done by Boullay,[1] who in 1827 announced, as the result of his work, the existence of the two salts $PbI_2.KI$ ($KPbI_3$) and $PbI_2.4KI$ (K_4PbI_6). The last named salt forms a very marked exception to the law of combination of the alkali halides with other halides. As the work of Boullay had been carried out quite a long time ago it was deemed advisable to repeat it, for at that time quantitative determinations were not so accurate as at present, and, furthermore, the filter-pump had not then been invented, so that the method of preparation of the salts must have been rather crude. The first efforts were therefore directed to the preparation of the salt $PbI_2.KI$ ($KPbI_3$) described by Boullay. The potassium iodide used in these experiments was purified by decomposing any iodate present by zinc amalgam.[2] The lead iodide first used was prepared by precipitating a solution of pure lead nitrate with pure potassium iodide solution. Towards the latter part of the investigation commercial lead iodide, prepared by A. L. Thomsen & Co., of Baltimore, was used. This gave results agreeing very closely with those obtained by using the lead iodide prepared for the purpose.

According to Boullay, when a solution of lead nitrate is added to a slightly concentrated solution of potassium iodide there is formed at first a red precipitate of lead iodide which soon turns white, owing to the conversion of the lead iodide into the double

[1] Ann. chim. phys. [2], **34**, 366.

[2] Am. Chem. J. **10**, 321.

salt $PbI_2.KI$ ($KPbI_3$) by the potassium iodide present in the solution. Great trouble was experienced at first in preparing this salt. Boullay directed to use a solution of potassium iodide only slightly concentrated. In each of the preliminary experiments lead iodide was precipitated when a solution of lead nitrate was added to a solution of potassium iodide only slightly concentrated; but, on standing, whether cold or hot, there was no change to a white color as described by Boullay. But when a solution of potassium iodide slightly more concentrated was used and heat applied, it was noticed that yellow needles formed along the upper portion of the beaker in which the experiment was being conducted, where drops of the solution had spattered, these drops becoming more concentrated by evaporation. This observation suggested that if a more concentrated solution of potassium iodide were used the salt might be obtained. Experiments were then made to determine the exact conditions under which the salt is formed. To this effect a solution of lead nitrate was prepared so that 1 cc. should contain 0.25 gram of salt. Likewise a solution of potassium iodide was prepared so that 1 cc. should contain 0.25 gram of salt. Five portions of the lead nitrate solution of 5 cc. each were then measured out. To these were added quantities of potassium iodide solution (warm) varying from 5 cc. to 25 cc. Lead iodide was precipitated in each case, but on cooling the mass did not turn white, as described by Boullay, in any of the five portions. So to five portions more (5 cc. each) of the potassium iodide solution were added successively quantities of solid potassium iodide varying from 0.25 gram to 1.25 gram. These portions were heated and added to 5 cc. portions of the lead nitrate solution. Lead iodide was precipitated in each case, but still there was no double salt formed; so, again to five portions (5 cc. each) of the potassium iodide solution were added quantities of solid potassium iodide varying from 3 grams to 5 grams. The solutions were then heated and added to five portions (5 cc. each) of the lead nitrate solution. Lead iodide was precipitated in each case, but gradually the red precipitate became white, the most concentrated solution becoming white first. On heating, the white salt was decomposed and insoluble lead iodide remained, having the form of the original crystals; but, on cooling, the crystals again became white, owing to the formation of the double salt, as described by Boullay. This

slightly yellowish salt was freed from the mother-liquor as much as possible by means of a filter-pump, then pressed between drying paper and placed in a desiccator for twelve hours. On analysis this salt showed:

I. 0.9779 gram salt lost 0.0111 gram H_2O.

II. 1.6154 gram salt gave 0.7023 gram $PbSO_4$ = 0.4797 gram Pb.

III. 1.0204 gram salt, after standing over sulphuric acid one week, lost 0.0028 gram.

	Calculated for $KPbI_3$ ($PbI_2.KI$).	Found. I.	II.	III.
Pb	33.02	...	29.70	...
H_2O	...	1.14	...	0.273

Plainly this salt lost its water of crystallisation by standing over sulphuric acid, a dehydrating agent, and therefore should not be dried in this way. From the mother-liquor of this salt there crystallised after twelve hours long needles of slightly yellowish tint. By a slight elevation of temperature these needles are redissolved in the mother-liquor, but by rapidly heating the beaker containing the mass with a free flame the needles are decomposed, lead iodide remaining, which retains the form of the original crystals. On cooling these needles again became white. The explanation of the formation of these long needles in the mother-liquor will be given under the head of the salt $K_4Pb_3I_{10}.6H_2O$ ($3PbI_2.4KI.6H_2O$).

The salt $KPbI_3$ ($PbI_2.KI$) was then prepared in larger quantities by using the following proportions: 4 grams of lead nitrate were dissolved in 15 cc. of water; likewise 15 grams potassium iodide were dissolved in 15 cc. of water. The latter solution was then heated and added to the lead nitrate solution, cooled rapidly, stirring all the while. The double salt thus formed was pumped dry and pressed between drying paper for twenty-four hours. On analysis this salt showed:

I. 1.3640 gram salt lost 0.0712 gram H_2O.

II. 1.1614 gram salt lost 0.0610 gram H_2O.

III. 1.0744 gram salt gave 0.4842 gram $PbSO_4$ = 0.3307 gram Pb.

IV. 1.3640 gram salt gave 0.6162 gram $PbSO_4$ = 0.4209 gram Pb.

V. 0.8867 gram salt gave 0.4002 gram $PbSO_4$ = 0.2733 gram Pb.

	Calculated for $KPbI_3.2H_2O$.	I.	II.	Found. III.	IV.	V.
Pb	31.23	...	...	30.78	30.86	30.82
H_2O	5.43	5.22	5.25	...	...	...

This was evidently the salt $KPbI_3.2H_2O$. Boullay prepared this salt, but dried it over lime; accordingly he found only 3 per cent. H_2O, and says:[1] "Si l'on suppose que, dans ce sel, les deux iodures soient à l'état d'hydriodates, il foudrait 4.16 l'eau pour 100 parties du sel humide; je n'en ai trouvé que 3.00."

In speaking of the formation of this salt, Boullay states that it is always formed when a slightly concentrated solution of potassium iodide is brought together, hot or cold, with an *excess of lead iodide*. It is difficult to understand why he should have made this statement, as it is evident from his work on the subject that he never worked with an excess of lead iodide, but that in each case lead iodide was first precipitated, and this was then converted into the double salt, or rather iodoplumbite, by the excess of potassium iodide in the solution. However, in order to test his statement strictly, a solution of potassium iodide not quite saturated at 20° was added to a large excess of lead iodide in a beaker and stirred thoroughly. On first cooling, the excess of lead iodide collected at the bottom of the vessel, while the supernatant liquid remained clear; but on the following day silky, needle-shaped crystals were found in the solution and also mixed with unchanged lead iodide in the bottom of the vessel. The best crystals were removed from the solution, dried and analysed, giving the following results:

I. 0.2150 gram salt gave 0.0957 gram $PbSO_4$ = 0.0654 gram Pb.

	Calculated for $KPbI_3.2H_2O$.	Found.
Pb	31.23	30.42

This was therefore the same salt as had been previously prepared.

Some of the needle-shaped crystals of the salt $KPbI_3.2H_2O$ were then heated to 140° to test whether any more water could be driven off than at 110°, but no greater loss of weight was found. So there are only two molecules of water of crystallisation present in the salt. The farther effect of heat upon this salt was tried in this way. Some of the needle-shaped crystals were placed in an ignition tube; this in turn was placed in a sulphuric acid bath and the temperature raised gradually. At 70° water began to be given off, the salt becoming a brighter yellow and decreasing considerably in bulk. As the temperature was raised the amount

[1] Ann. chim. phys. [2], **34**, 367.

of water given off increased to such an extent that it collected in large drops on the side of the tube. These drops falling on the salt below decomposed it instantly, as was shown by the color of the lead iodide which appeared. Thus the same water which had been present in the compound as water of crystallisation, after having been once driven out by heat, served to decompose the anhydrous salt when brought into contact with it. By using an ignition tube, bent at an angle in order to prevent the water falling back upon the salt, it was found that at about 310° the salt decomposed, iodine being given off. Treated with absolute alcohol, this salt is decomposed just as when treated with water.

II. *Salt of the composition* K_4PbI_6 ($PbI_2.4KI$). — While attempting to determine the concentration at which the salt $KPbI_3.2H_2O$ was formed, as mentioned above, efforts were made to prepare the salt K_4PbI_6 ($PbI_2.4KI$) described by Boullay[1] under the head of "Bibasic iodoplumbate of iodide of potassium." He obtained it by adding lead iodide to a concentrated solution of potassium iodide, this last being in excess. He represented the composition of the salt by the formula "$2KaI_4 + PbI_4$," or, according to the present atomic weights, $PbI_2 + 4KI$. This formula was based upon the following analyses:

	Found.		Calculated for
	I.	II.	$PbI_2 + 4KI$.
PbI_2	34.0	36.0	41.0
KI	66.0	64.0	59.0

Efforts were then directed to repeating this work in order to see whether the salt could actually be formed; for if it does exist it forms a very striking exception to the law of combination of alkali halides with other halides mentioned in the introduction. To a cold saturated solution of potassium iodide lead nitrate was added, and a yellowish white salt was obtained. This was the first compound of lead and potassium iodides obtained during the course of the investigation, and was dried not by pumping off the mother-liquor, but by simple filtration, then pressing between drying paper for a short while, and finally completely dried by standing over lime, the method adopted by Boullay.

On analysis this salt showed:

I. 1.2961 gram salt lost 0.0388 gram H_2O.

II. 1.2734 gram salt lost 0.0191 gram H_2O.

[1] Ann. chim. phys. [2] **34**, 370.

III. 0.3880 gram salt gave 0.1435 gram $PbSO_4$ = 0.0980 gram Pb.

IV. 2.3640 grams salt gave 0.9015 gram $PbSO_4$ = 0.6157 gram Pb.

	Calculated for $PbI_2.4KI$.	Found. I.	II.	III.	IV.
Pb	18.40	...	...	25.26	26.04
H_2O	...	2.99	1.50	...	...

These results plainly show that the salt K_4PbI_6 ($PbI_2.4KI$) had not been obtained, but rather a salt approaching in composition the salt $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$) described by Ditte,[1] with the exception of the water, which showed by the difference in the two analyses, the second having been made several days after the first, that water was abstracted by the lime over which the salt stood. The preparation of this salt and its analyses were rather crude, as they were the first attempts; however, the results were sufficient to show that the salt K_4PbI_6 ($PbI_2.4KI$) had not been obtained under the conditions described by Boullay. Later in the investigation another attempt was made to prepare the salt, following the directions of Boullay, with the exception that the salt, instead of being dried over lime, was pressed for several days between drying paper. On analysis this salt showed:

I. 1.2106 gram salt lost 0.0634 gram H_2O.

II. 0.9371 gram salt lost 0.0490 gram H_2O.

III. 1.0085 gram salt gave 0.4569 gram $PbSO_4$ = 0.3121 gram Pb.

IV. 0.8693 gram salt gave 0.3914 gram $PbSO_4$ = 0.2673 gram Pb.

	Calculated for K_4PbI_6.	$KPbI_3.2H_2O$.	Found. I.	II.	III.	IV.
Pb	18.40	31.23	...	...	30.95	30.75
H_2O	...	5.43	5.24	5.23	...	...

The salt was evidently the salt $KPbI_3.2H_2O$. These last results differed very widely from those first obtained in trying to prepare the salt K_4PbI_6; in the first case the percentage of lead was 25.26, in the second case 30.95. Many efforts were then made to obtain the salt which showed 25.26 per cent. of lead, varying the conditions in all possible ways, but in no case was a salt obtained even approaching this composition. Therefore it seems justifiable to conclude that the salt yielding 25.26 per cent.

[1] Ann. chim. phys. [5] 24, 226.

of lead, which was prepared and analysed in a rather rough way, must have been very impure, owing to excess of potassium iodide present. From the above facts it appears to follow that the salt K_4PbI_6 ($PbI_2.4KI$) does not exist, and that the mass which Boullay considered to have this composition was really a mixture of the salt $KPbI_3.2H_2O$ with a large excess of potassium iodide.

III. *Salt of the composition* K_5PbI_7 ($PbI_2.5KI$).—A salt of this composition is mentioned in Graham-Otto's "Lehrbuch der anorganischen Chemie," and is ascribed to Boullay, but no reference is given to the article in which Boullay describes this salt. All the articles of Boullay on the combinations of lead and potassium iodides were then carefully examined, but no such salt could be found. A careful search was then made through Berzelius' Jahresbericht and the Jahresbericht now published, but no trace of the salt could be found. However, in order to make the proof of its non-existence more positive, all the journals in the chemical library of the Johns Hopkins University were carefully examined. This work consumed about two months' time, and as a result of it, no description of the salt K_5PbI_7 ($PbI_2.5KI$) or its method of preparation could be found. Furthermore, in all the experiments on the combinations of lead iodide with potassium iodide there was found at no time a salt whose composition approached in any degree that represented by the formula K_5PbI_7 ($PbI_2.5KI$). Therefore it is most probable that this is an error in Graham-Otto's "Lehrbuch der anorganischen Chemie."

IV. *Salts of the composition* $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$) and $K_2PbI_4.2H_2O$ ($PbI_2.2KI.2H_2O$).—Since the paper published by Boullay in 1827, the principal work on the double iodides of lead and potassium has been done by Ditte, and also by Berthelot. Ditte[1] described the salt $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$), giving an account of its method of formation, appearance and general behavior, and studied its decomposition by water.

Berthelot[2] then took up the subject and described the two salts. $K_2PbI_4.2H_2O$ ($PbI_2.2KI.2H_2O$) and $K_4Pb_3I_{10}.6H_2O$ ($3PbI_2.4KI$, $6H_2O$). The investigation was then directed to the repetition of the work of these chemists. Both agree that the salt containing lead and potassium iodides, in the proportion of one part of lead iodide to two parts of potassium iodide, is formed whenever lead iodide is added to a warm solution of potassium iodide and

[1] Ann. chim. phys. [5], **24**, 226. [2] Ann. chim. phys. [5], **29**, 289.

the solution allowed to cool. Ditte states that the salt is formed also in the cold.

As previously stated, when this investigation was first begun a salt was obtained which seemed to have the composition $K_2PbI_4 + H_2O$ ($PbI_2.2KI + H_2O$), the water of crystallisation not being constant. But now, on the first attempt to repeat the work of Ditte, a salt was obtained resembling in appearance that described by him, but on analysis it gave the following results:

I. 1.2227 gram salt lost 0.0413 gram H_2O.

II. 2.1526 grams salt gave 0.9541 gram $PbSO_4$ = 0.6517 gram Pb.

III. 0.9733 gram salt gave 0.4296 gram $PbSO_4$ = 0.2934 gram Pb.

	Calculated for		Found.		
	$K_2PbI_4.4H_2O$.	$KPbI_3.2H_2O$.	I.	II.	III.
Pb	23.93	31.23	...	30.28	30.14
H_2O	8.33	5.43	3.38	...	...

Evidently this salt agreed more closely with the formula $KPbI_3.2H_2O$ than $K_2PbI_4.6H_2O$. The water of crystallisation varied in this salt, as it was dried over lime, as was the case with several of the preceding salts. The salt just mentioned was prepared from a hot solution. Now, as it had been shown earlier that heat decomposed the salt $KPbI_3.2H_2O$ with a separation of lead iodide, it was thought probable that the salt $K_2PbI_4.4H_2O$ might be prepared in the cold. To this end 15 cc. of a cold saturated solution of potassium iodide was added to 10 cc. of a cold saturated solution of lead nitrate. The lead iodide first precipitated soon turned white, owing to the formation of the double salt. The mass having become quite pasty, more of the potassium iodide solution was added, enough to render the mass quite mobile and to insure all lead iodide being converted into the double salt. The salt prepared in this way was analysed by boiling with sodium carbonate, the lead iodide in this way being changed to the carbonate. This was then filtered through a Gooch crucible, washed thoroughly and ignited at a low red heat. The lead was then weighed as oxide. Analysed in this way the following results were obtained:

I. 1.7823 gram salt lost 0.0966 gram H_2O.

II. 1.6530 gram salt lost 0.0892 gram H_2O.

III. 1.7823 gram salt gave 0.5990 gram PbO = 0.5560 gram Pb.

	Calculated for $K_2PbI_4.4H_2O$.	Calculated for $KPbI_3.2H_2O$.	Found. I.	Found. II.	Found. III.
Pb	23.93	31.23	...	...	31.20
H_2O	8.33	5.43	5.42	5.39	...

As the effort to prepare the salt $K_2PbI_4.4H_2O$ in the cold had failed, it was then attempted to prepare it by heating a cold saturated solution of potassium iodide almost to boiling, then adding lead iodide to saturation; but this was found impracticable, since such large quantities of lead iodide are taken up by the solution that the double salt begins to separate from the solution at the surface while lead iodide is still being dissolved. So to a hot solution of potassium iodide (cold saturated) lead iodide was added in large quantities, but not enough to cause the separation of the double salt, as mentioned above. On cooling, pale yellow needles separated. These were dried and marked No. 1. The filtrate from this salt was moderately diluted with water, and soon light-colored needle-shaped crystals were seen to appear. On standing for a short time the whole mass became almost solid, owing to the thick network of crystals formed. These were dried and marked No. 2. By continuing the dilution crystals again began to appear, but now on adding more water these crystals were decomposed into lead iodide and potassium iodide. However, on stirring the mass thoroughly the original white color was restored. These crystals were dried and marked No. 3. By further dilution of the filtrate still another crop of crystals were obtained. These were dried and marked No. 4. But now on adding water to a small portion of the filtrate decomposition took place immediately, lead iodide separating in large quantities. But on treating another portion of the filtrate with alcohol a flocculent white salt separated, which on close examination seemed to be composed of little needles. These were dried and marked No. 5. It was thought that these five salts would prove to be a series of compounds showing a gradation in composition. On analysis these salts showed:

I. 1.5388 gram of salt No. 1 lost 0.0813 gram H_2O, and 1.6216 gram of salt No. 1 gave 0.7300 gram $PbSO_4$ = 0.4986 gram Pb.

II. 1.2032 gram salt No. 2 lost 0.0617 gram H_2O, and 1.1969 gram salt No. 2 gave 0.5391 gram $PbSO_4$ = 0.3682 gram Pb.

III. 1.2780 gram salt No. 3 lost 0.0673 gram H_2O and gave 0.5782 gram $PbSO_4$ = 0.3949 gram Pb.

IV. 1.1226 gram salt No. 4 lost 0.0590 gram H_2O and gave 0.5096 gram $PbSO_4 = 0.3481$ gram Pb.

V. 1.2413 gram salt No. 5 lost 0.0639 gram H_2O and gave 0.5637 gram $PbSO_4 = 0.3850$ gram Pb.

	Calculated for $KPbI_3.2H_2O$.	Found. I.	II.	III.	IV.	V.
Pb	31.23	30.75	30.76	30.90	31.01	31.02
H_2O	5.43	5.28	5.13	5.27	5.26	5.15

The results here, as in almost all of the analyses, are below the theoretical. This is to be expected, as the mother-liquor, which is rich in potassium iodide, cannot be washed from the salts, but has to be removed by pressing between drying paper. This would plainly give low results for water and lead, and at the same time high results for iodine and potassium.

An examination of the above results shows that instead of obtaining a series of salts the same salt was obtained in every case, becoming gradually purer as the solution was diluted. Boullay observed this same phenomenon. These facts also show that the same salt, $KPbI_3.2H_2O$, is obtained, and not the salt $K_2PbI_4.4H_2O$, described by Ditte, whether a hot concentrated or a cold solution of potassium iodide be used, decreasing from considerable concentration to just above the point where separation of lead iodide takes place; and still further, alcohol separates the same salt from this last most dilute solution. This is very strong evidence against the existence of the salt $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$), described by Ditte, or $K_2PbI_4.2H_2O$ ($PbI_2.2KI.2H_2O$), described by Berthelot.

Another solution was then prepared similar to that from which the salt marked No. 1 had been obtained, but instead of filtering from the crystals formed, water was added. Lead iodide at first separated, but by stirring the mass thoroughly the original color was restored. In this way a large quantity of water was added, until finally, by further addition of water to a small portion of the mass, lead iodide was seen to separate, and remained so on stirring thoroughly. The analysis of the salt thus formed proved it to be the salt $KPbI_3.2H_2O$.

Efforts were then made to prepare the salt $K_2PbI_4.4H_2O$ by dissolving the salt $KPbI_3.2H_2O$ in a large excess of a cold saturated solution of potassium iodide. On heating the salt dissolved and on cooling, long needle-shaped crystals separated, similar in

appearance to the salt which had been dissolved. On analysis this salt showed:

I. 1.0974 gram salt gave 0.4942 gram $PbSO_4$ = 0.3375 gram Pb.

	Calculated for $KPbI_3.2H_2O$.	Found.
Pb	31.23	30.75

All of these attempts to prepare the salt described by Ditte and Berthelot having failed, it was concluded to try once again, following the directions of Ditte[1] exactly. In this way a salt was prepared which, when heated before being separated from its mother-liquor, decomposed; the lead iodide so formed retained the form of the original crystals. On filtering now and allowing to cool, a network of needle-shaped crystals was obtained which almost solidified the mass. On analysis this salt gave the following results:

I. 1.2172 gram salt lost 0.0650 gram H_2O.

II. 0.8487 gram salt gave 0.3836 gram $PbSO_4$ = 0.2620 gram Pb.

	Calculated for		Found.	
	$KPbI_3.2H_2O$.	$K_2PbI_4.4H_2O$.	I.	II.
Pb	31.23	23.93	...	30.87
H_2O	5.43	8.33	5.34	...

This was evidently the same salt which had been obtained in all the previous experiments.

Ditte[2] describes another method for the preparation of the salt $K_2PbI_4.4H_2O$; therefore, as all previous efforts to prepare the salt had failed, it was thought that by this means the salt might be obtained, or, on the other hand, very conclusive evidence that the salt does not exist.

This method of preparation consists in mixing freshly precipitated lead carbonate with an excess of a cold saturated solution of potassium iodide. No action takes place at ordinary temperatures, but on passing a current of carbon dioxide through the mixture for about twenty minutes the white lead carbonate is replaced by the yellowish crystals of the double salt. A salt prepared in this way gave on analysis the following results:

I. 0.9316 gram salt lost 0.0492 gram H_2O.

II. 1.0653 gram salt gave 0.4908 gram $PbSO_4$ = 0.3352 gram Pb.

III. 0.8595 gram salt gave 0.3958 gram $PbSO_4$ = 0.2703 gram Pb.

[1] Ann. chim. phys. [5], **24**, 226.

[2] Ann. chim. phys. [5], **24**, 235.

	Calculated for $KPbI_3.2H_2O$.	Found. I.	II.	III.
Pb	31.23	...	31.47	31.45
H_2O	5.43	5.28	...	...

So this method for the preparation of the salt $K_2PbI_4.4H_2O$ also failed.

The salt $K_2PbI_4.2H_2O$ described by Berthelot[1] was obtained, to use his own words, "par le froidissement de la solution de l'iodure de plomb dans une solution concentrée d'iodure de potassium." Plainly this condition has been tried repeatedly in the effort to prepare the salt $K_2PbI_4.4H_2O$ (Ditte), but in order to be absolutely certain that this salt of Berthelot could not be prepared, three successive attempts were made, varying the conditions slightly in each case. The salts obtained in this way gave on analysis the following results:

I. 1.0975 gram salt No. 1 lost 0.0565 gram H_2O, and 1.3778 gram salt No. 1 gave 0.6141 gram $PbSO_4$ = 0.4194 gram Pb.

II. 1.3876 gram salt No. 2 lost 0.0724 H_2O, and 0.6197 gram salt No. 2 gave 0.2738 gram $PbSO_4$ = 0.1870 gram Pb.

III. 0.9158 gram salt No. 3 lost 0.0477 gram H_2O, and 0.8046 gram salt No. 3 gave 0.3569 gram $PbSO_4$ = 0.2438 gram Pb.

	Calculated for $K_2PbI_4.2H_2O$.	$KPbI_3.2H_2O$.	Found. I.	II.	III.
Pb	24.97	31.23	30.44	30.18	30.30
H_2O	4.35	5.43	5.15	5.22	5.21

The results show that all three salts have the composition $KPbI_3.2H_2O$. Solutions of potassium iodide saturated at 100° were then used, but were soon found to be of no value, as, when a rather small quantity of lead iodide was added, on cooling, a large mass of potassium iodide crystallised out along with the double salt; and when a large quantity of lead iodide was added the mass soon became unmanageable, on account of the large amount of double salt present in the solution, so that it could not be filtered or purified in any way.

From all of the above facts it is to be concluded that the salts $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$) and $K_2PbI_4.2H_2O$ ($PbI_2.2KI.2H_2O$) cannot exist; for not only have the directions of both Ditte and Berthelot been closely followed, but, furthermore, the conditions have been changed, using at one time hot solutions, at another cold, at

[1] Ann. chim. phys. [5], 29, 289.

one time cold saturated, at another dilute; again a solution of potassium iodide saturated at 100° was employed, and in every case the salt $KPbI_3.2H_2O$ was obtained. Further, the attempt was made to obtain the salt by dissolving the salt $KPbI_3.2H_2O$ in a cold saturated solution of potassium iodide, and finally by passing carbon dioxide through a mixture of lead carbonate and potassium iodide solution, and here likewise was obtained the salt $KPbI_3.2H_2O$.

V. *Salt of the composition* $K_4Pb_3I_{10}.6H_2O$ ($3PbI_2.4KI.6H_2O$).—This salt was described by Berthelot.[1] He in turn ascribes it to Boullay, but gives no reference to any article by Boullay. Accordingly, careful search was made for Boullay's description of this salt while looking for his account of the salt K_5PbI_7 ($PbI_2.5KI$), mentioned on page 3, but this search was unsuccessful.

Berthelot states that it is formed by slow cooling of the mother-liquor from the salt $K_2PbI_4.2H_2O$, which, in turn, is prepared by adding lead iodide to a concentrated solution of potassium iodide. These directions were closely followed. The mother-liquor from the salt which first separated on cooling was surrounded by water in order to lower the temperature, and was then allowed to stand four days. Long, yellow needles separated which on analysis gave the following results:

I. 0.7839 gram salt lost 0.0382 gram H_2O.

II. 0.9913 gram salt gave 0.4012 gram $PbSO_4$ = 0.2740 gram Pb.

	Calculated for $K_4Pb_3I_{10}.6H_2O$.	Calculated for $K_3Pb_2I_9.4H_2O$.	Found. I.	Found. II.
Pb	28.82	27.75	...	27.64
H_2O	5.02	4.83	4.87	...

This analysis seemed to show that the salt had the composition $K_3Pb_2I_9.4H_2O$ ($2PbI_2.3KI.4H_2O$). In order to confirm this the experiment was repeated. The mother-liquor in this case was surrounded by ice. Long needles crystallised from the solution, but in addition, considerable quantities of potassium iodide also separated. So the whole was heated gently until all had passed into solution. The beaker was then allowed to cool. The following night was very cold, and on examining the beaker the next morning there could be seen both the double salt and potassium iodide. This was heated again until all dissolved, and after several trials at different temperatures, finally a good crop of long

[1] Ann. chim. phys. [5], **29**, 289.

needle-shaped crystals was obtained which were apparently free from potassium iodide. This salt on analysis showed:

I. 1.2129 gram salt lost 0.0647 gram H_2O.

II. 0.6945 gram salt gave 0.3140 gram $PbSO_4$ = 0.2145 gram Pb.

	Calculated for $KPbI_3.2H_2O$.	Found. I.	Found. II.
Pb	31.23	...	30.88
H_2O	5.43	5.33	...

These results showed that most probably in the first preparation of the salt the temperature was reduced too low, so that the salt was mixed with potassium iodide. In order to test this view and confirm the last experiment the work was very carefully repeated, accurate measurements being made at each stage, as follows: 100 cc. of a solution (saturated at 22°) was heated. When the temperature reached 75° lead iodide was added gradually while the temperature was being raised to 100°. In this way 17.5084 grams were added. The solution was then allowed to cool. At 34° needle-shaped crystals began to separate. The cooling was continued until the temperature reached 22°. The mother-liquor was then pumped off and placed under a bell-jar, where it was allowed to stand three days, the temperature varying only slightly above or below 18°. Long, needle-shaped crystals separated as before, and apparently free from potassium iodide. On analysis this salt showed:

I. 0.9263 gram salt lost 0.0474 gram H_2O.

II. 1.2400 gram salt gave 0.5548 gram $PbSO_4$ = 0.3789 gram Pb.

	Calculated for $K_4Pb_3I_{10}.6H_2O$.	Calculated for $KPbI_3.2H_2O$.	Found. I.	Found. II.
Pb	28.82	31.23	...	30.56
H_2O	5.02	5.43	5.12	...

From these facts it seems probable that the salt described by Berthelot as $3PbI_2.4KI.6H_2O$ ($K_4Pb_3I_{10}.6H_2O$) was really a mixture of the salts $KPbI_3.2H_2O$ and potassium iodide. Indeed this is rendered quite probable when it is remembered that at the temperature and concentration used the potassium iodide, which is present in the solution in large excess, separates very easily, as has already been shown.

Sodium Iodoplumbite.

The literature in regard to this subject is extremely limited.

Boullay[1] states that it is probable that the other alkali iodides would act like potassium iodide in regard to the formation of the double halide, but makes no experiments on the subject. Ditte[2] dismisses the subject by stating that sodium iodide behaves like potassium iodide, but gives no experimental data. Poggiale[3] mentions a double iodide of lead and sodium, to which he ascribes the formula $PbI_2.NaI$ ($NaPbI_3$), but this work is not at all reliable. Efforts were then made to obtain this salt so that it could be analysed and its composition determined. To this effect 100 grams of sodium iodide were dissolved in 75 cc. water at 20°. Lead iodide was then added until no more would dissolve, about 60 grams being thus added. This solution, on standing, gave birth to no crystals. The double salt is therefore much more soluble than the corresponding potassium salt. The solution was then heated and 10 grams more of lead iodide added. On cooling, nothing crystallised out, so the solution was then evaporated to about two-thirds of its former volume. On cooling, small needle-shaped crystals separated, closely resembling in appearance the potassium salt. These crystals formed in such large quantities that the mass almost completely solidified. Like the potassium salt this salt is decomposed by water and also by heat with a separation of lead iodide. Great difficulty was experienced in purifying this salt, for such large quantities of sodium iodide were mixed with it. Various methods for purification were tried; for example, as sodium iodide is very deliquescent, it was hoped that by allowing the mixture to stand exposed to moist air enough water would be taken up to dissolve the sodium iodide and leave the double salt behind, but this proved unavailable. The method finally adopted was as follows: The mixture was exposed to the air until quite a considerable quantity of water had been absorbed. The undissolved portion, on being pressed with a stirring rod, appeared to consist of hard granular crystals, due to the sodium iodide present. A gentle heat was then applied, and it was soon found that the granular crystals had disappeared, a bright yellow salt remaining in the solution. The heating was now discontinued and the mass filtered rapidly by means of a filter-pump (for if the heating be continued the whole passes into solution). The salt was then pressed between drying

[1] Ann. chim. phys. [2], **34**, 372. [2] Compt. rend. **92**, 1343.
[3] J. prakt. Chem. **35**, 329.

paper for several days, and at the end of that time was found to be still moist, showing that the salt itself was deliquescent. It was then dried in an air-bath at 110°. The anhydrous salt, which is reddish yellow, gave on analysis the following results:

I. 0.8511 gram salt gave 0.4326 gram $PbSO_4$ = 0.2955 gram Pb.

	Calculated for $NaPbI_3$.	Found.
Pb	33.89	34.71

The composition of the salt is therefore very probably $NaPbI_3$. Nothing definite can be said in regard to the water of crystallisation, as the salt is so deliquescent that it cannot be obtained dry at ordinary temperatures. However, it is very probable that the salt does contain water of crystallisation from its analogy to the potassium salt and from the fact that so much sodium iodide crystallises out along with the double salt, the solution becoming very concentrated, probably because of so much water being taken up by the lead and sodium iodide to form water of crystallisation in the double salt.

Potassium Bromoplumbite.

The only work on this subject up to the present time is that done by Berthelot.[1] This was very unsatisfactory, however, and indeed he remarks that the substances obtained by him are not to be regarded as true chemical compounds, but as mixtures of the double salt with potassium bromide or lead bromide. He gives, however, the composition of one salt obtained as $3PbBr_2.2KBr$. Efforts were then made to determine whether a definite compound of lead and potassium bromides could be obtained. It was found that if to a solution of potassium bromide (saturated at 20°) a solution of lead nitrate (saturated at 20°) be added drop by drop, the lead bromide so formed was dissolved on constant stirring until quite a large quantity had been dissolved, though not nearly so large a quantity as in the case of the iodides. When all the lead bromide possible had been dissolved the solution was allowed to stand, and in about three hours colorless crystals began to be formed. After several days these tabular crystals grew to considerable size. The finely powdered salt gave on analysis the following results:

I. 0.7823 gram salt lost 0.0276 gram H_2O.

II. 1.1592 gram salt lost 0.0404 gram H_2O.

[1] Ann. chim. phys. [5] **29**, 293.

III. 1.2551 gram salt gave 0.7497 gram $PbSO_4 = 0.5120$ gram Pb.

IV. 0.9297 gram salt gave 0.5570 gram $PbSO_4 = 0.3804$ gram Pb.

	Calculated for $KPbBr_3.H_2O$.	Found. I.	II.	III.	IV.
Pb	41.06	...	...	40.80	40.92
H_2O	3.57	3.53	3.49	...	...

This salt was prepared repeatedly afterwards and the analyses leave no doubt that the composition is $KPbBr_3.H_2O$. The crystal form in every case was the same.

Similar efforts were made to prepare the corresponding sodium bromoplumbite, but all failed. It was thought at one time that the salt had been obtained as lath-shaped crystals separated from the solution of lead bromide in sodium bromide. This salt, however, proved on analysis to be lead bromide. Efforts were also made to prepare the salt by using a hot sodium bromide solution, but the salt which separated on cooling proved to be lead bromide. Undoubtedly the salt is formed in solution, but as yet it has been found to be impossible to isolate it.

Potassium Chloroplumbite.

Similar statements are made by Berthelot[1] in regard to this salt as in the case of the bromoplumbite and equally as indefinite. Strohecker[2] also mentions the existence of double salts of lead and potassium chlorides, but gives no formulas.

The investigation was then turned to the preparation of this salt, potassium chloroplumbite. A cold saturated solution of potassium chloride was heated to boiling and a solution of lead nitrate (cold saturated) added drop by drop, the mass being continually stirred. Lead chloride was dissolved, but not so much of the lead salt as in the case of the iodide and bromide. On cooling a salt crystallised out in fine white needles, which on analysis gave the following results:

I. 1.2142 gram salt gave 1.0281 gram $PbSO_4 = 0.7022$ gram Pb.

II. 1.2039 gram salt gave 1.0176 gram $PbSO_4 = 0.6950$ gram Pb.

	Calculated for $KPbCl_3$.	Found. I.	II.
Pb	58.71	57.81	57.73

[1] Ann. chim. phys. [5] 29, 293.

[2] Jahresbericht, 1863, 282.

There is no water of crystallisation in this salt. Instead of cooling the solution rapidly, as was done above, if it be cooled slowly and kept at about 35° the potassium chloroplumbite can be obtained in lenticular crystals, somewhat needle-shaped. These crystals have the same composition as the above analysed salt, but they contain some water mechanically held in the crystals, for on heating to about 200° the salt decrepitates just as potassium chloride does when heated. This salt is necessarily impure on account of the large excess of potassium chloride present in the solution.

All efforts to prepare the sodium chloroplumbite failed. A salt crystallising in radiating leaflets was obtained, but this by analysis was proved to be lead chloride.

The work on the fluorplumbites could not be carried to any extent on account of lack of time, but a few qualitative experiments showed that if a cold saturated solution of lead nitrate be added to a cold saturated solution of potassium fluoride, heated almost to boiling, a small portion of the lead fluoride so formed is dissolved. However, less of the lead salt is dissolved in this case than in the case of either the iodide, bromide, or chloride.

It was hoped that the investigation could be extended to the mixed halides, but want of time prevented this.

Conclusion.

The principal results of this investigation may be summed up as follows:

I. Of the six iodoplumbites of potassium described by Boullay, Ditte and Berthelot, only one exists. This is the salt $KPbI_3.2H_2O$.

II. The bromoplumbite of potassium is a well crystallised compound, having the composition $KPbBr_3.H_2O$.

III. The chloroplumbite of potassium can also be prepared in well formed crystals, and has the composition $KPbCl_3$.

IV. The quantity of the lead halide dissolved in the alkaline halide increases with the atomic weight of the halogen. Thus only a small quantity of lead fluoride dissolves in a solution of potassium fluoride, a larger quantity of lead chloride in potassium chloride solution, a still larger quantity of lead bromide in potassium bromide solution, and greatest of all, lead iodide in potassium iodide solution.

V. The corresponding sodium salts, if formed, are separated with great difficulty, as in the case of the iodoplumbite, while no salt was isolated in the case of the sodium bromo or chloroplumbite.

VI. All these salts are decomposed by water, and in order that they may exist in solution a certain minimum amount of alkali halide must be present, this amount varying inversely as the atomic weight of the halogen atom present in the compound.

VII. The amount of the water of crystallisation decreases with the atomic weight of the halogens, thus: $KPbI_3.2H_2O$, $KPbBr_3.H_2O$, and $KPbCl_3$.

VIII. Finally, it is seen that the composition of all these salts allows them to be expressed by formulas in which two halogen atoms play the part of the so-called linking oxygen atom, thus proving these salts to be no exception to the law of combination of alkali halides with other halides put forward by Professor Remsen and mentioned in the introduction to this investigation. These salts are to be represented thus:

$$KPbI_3.2H_2O \text{ or } Pb<^{I}_{(I_2)K} + 2H_2O,$$

$$KPbBr_3.H_2O \text{ or } Pb<^{Br}_{(Br_2)K} + H_2O, \text{ and}$$

$$KPbCl_3 \text{ or } Pb<^{Cl}_{(Cl_2)K}.$$

A possible explanation of the results obtained by Boullay, Ditte and Berthelot is this: In preparing the iodoplumbites two salts are used, lead iodide and potassium iodide, neither of which contains any water of crystallisation. Now, the iodoplumbite of potassium contains two molecules of water of crystallisation, and if the solutions are concentrated, then in the formation of the iodoplumbite a large amount of this water is taken up as water of crystallisation. This would serve to concentrate the solution very much, and would thus cause a separation of potassium iodide, which is present in large excess in the solution. This would cause the analyses of the salts to show a much larger proportion of potassium iodide than actually belonged to the true compound.

Three other exceptions to the law of combination in double halides have been found, namely, $SnCl_2.4KCl.3H_2O$, described by Poggiale; $SbCl_3.6CsCl$, described by Godeffroy; and $CuCl.2KCl$ described by Mitscherlich. In regard to the salt $SnCl_2.4KCl$.

$3H_2O$, Mr. G. M. Richardson, working in this laboratory, has shown conclusively that this salt does not exist; and similarly, Mr. C. E. Saunders, also working in this laboratory, has shown that the salt $SbCl_3.6CsCl$ does not exist. Finally, in regard to the salt CuCl.2KCl, the evidence points, at present, to the correctness of this formula; but more work is still needed on this compound. This last salt, therefore, is the only real exception to the law as put forward by Professor Remsen.

BIOGRAPHICAL.

The author of this dissertation, Charles Holmes Herty, son of B. R. Herty, was born on the fourth day of December, 1867, in Milledgeville, Georgia. In 1879 he entered the Middle Georgia Military and Agricultural College at Milledgeville, Georgia, this being a branch of the State University. Here he spent five years, graduating on July 2d, 1884. In October of this year he entered the Junior class of the University of Georgia, at Athens, Georgia, graduating with the degree of Ph. B. on July 12th, 1886. In the following October he entered the Johns Hopkins University, where he has pursued the study of chemistry, mineralogy and geology.